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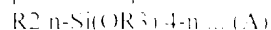
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CLAIMS

[Claims 0]

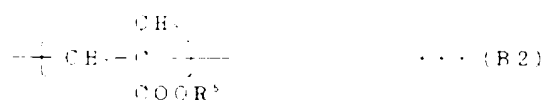
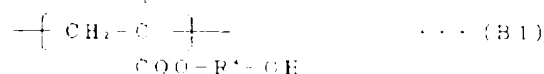
[Claim 1] To a plastics base-material front face, it is the following formula (A).

[Formula 1]



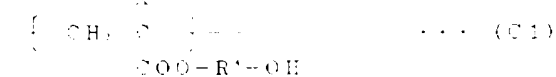
The inside R_2 of [], however a formula is the organic machine which has one or more bases chosen from the group which consists of the alkyl group of carbon numbers 1-4, a vinyl group or a meta-chestnut ROKISHI machine, the amino group, an epoxy group, and a sulphydryl group, R_3 is the alkyl group of carbon numbers 1-4, and n is the integer of 0-2. [the hydrolyzate (portion) of the alkoxy silane come out of and shown, its partial condensate or 1 - 40 % of the weight (weight criteria by $R_2 nSiO_{(4-n)/2}$ conversions) of such mixture, and the following formula (B1) -- and (B-2) --

[Formula 2]



The inside X of [], however a formula is a hydrogen atom or a methyl group, R_4 is the alkylene machine of carbon numbers 2-5, and R_5 is the alkyl group of carbon numbers 1-4. [The 1st layer which it comes out [layer], mainly consists [layer] of a repeating unit shown, and comes to carry out heat-of-reaction hardening of acrylic resin (199-60 % of the weight [whose mole ratios (p/q) of this repeating unit (B1) and (B-2) are 1 - 99 - 50/50] mixture or a reactant, the hydrolyzate (portion) of the alkoxy silane shown by the above-mentioned formula (A), its partial condensate or 40 - 90 % of the weight (weight criteria by $R_2 nSiO_{(4-n)/2}$ conversions) of such mixture, and the following formula (C1) -- and (C2) --

[Formula 3]



The inside X of [], however a formula is a hydrogen atom or a methyl group, R_4 is the alkylene machine of carbon numbers 2-5, and R_5 is the alkyl group of carbon numbers 1-4. [from the repeating unit come out of and shown -- mainly -- becoming -- this repeating unit (C1) -- and (C2) the 2nd layer which comes to carry out heat-of-reaction hardening of acrylic resin (1160-10 % of the weight [whose mole ratios (r/s) are 1 - 99 - 100/0] mixture or a reactant and the following formula (D)]

[Formula 4]

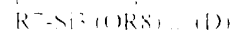


The inside R_9 of [], however a formula is the alkyl group of the carbon numbers 1-3 replaced by the alkyl group of carbon number 1-3, the vinyl group or the meta-chestnut ROKISHI machine, the amino group, and one or more bases chosen from the group which consists of a glycidoxy machine, R_{10} is the alkyl group of carbon numbers 1-4, and x is the integer of 0-2. [

The plastic-molding object protected in the front face which carries out the laminating of the 3rd layer which makes the organopolysiloxane resin which comes out and consists of the hydrolyzate (portion), its partial condensate, or such mixture of the alkoxy silane shown, come to heat-harden one by one from the 1st layer, and is characterized by the bird clapper.

[Claim 2] The 3rd layer is the following formula (D).

[Formula 5]



The inside R_7 of [], however a formula is the alkyl group of the carbon numbers 1-3 replaced by one or more bases chosen from the group which consists of the alkyl group, the vinyl group or the meta-chestnut ROKISHI machine, amino group, and

glycidoxy machine of carbon numbers 1-4, and R8 is the alkyl group of carbon numbers 1-4.] The plastic-molding object protected from the layer which made the organopolysiloxane resin which comes out and consists of the hydrolyzate (portion), its partial condensate or 90 - 30 % of the weight (weight criteria by $R7 \text{ SiO}_3 \cdot 2$ conversions) of such mixture, and 10 - 70 % of the weight of colloidal silica of the trialkoxysilane shown heat-harden in the front face according to claim 1 characterized by the bird clapper.

[Claim 3] The plastic-molding object protected in the front face according to claim 2 characterized by at least 70% of the weight of the trialkoxysilane used for constituting the 3rd layer being methyl trialkoxysilane.

[Claim 4] The plastic-molding object by which the alkoxysilane used for constituting the 3rd layer was protected from the tetrapod alkoxysilane not more than 40 mol %, and the trialkoxysilane beyond 60 mol % in the front face according to claim 1 characterized mainly by the bird clapper.

[Claim 5] The plastic-molding object protected in the front face according to claim 1 to 4 whose plastics base material is polycarbonate resin.

[Claim 6] The manufacture method of the plastic-molding object protected in the front face characterized by applying the constituent characterized by providing the following, making the 2nd layer form by heating subsequently, applying the constituent which contains an organopolysiloxane resin on this 2nd layer, and subsequently making the 3rd layer form by heating. On a plastics base material, they are the hydrolyzate (portion), its partial condensate, or such mixture of alkoxysilane. Apply the constituent containing mixture or a reactant with the acrylic resin which has a hydroxyl, the 1st layer is made to form by subsequently heating, and they are the hydrolyzate (portion), its partial condensate, or such mixture of alkoxysilane on this 1st layer. Mixture or a reactant with the acrylic resin which has a hydroxyl.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the plastic-molding object protected in the front face, and its manufacture method. Furthermore, surface hardness is related with the plastic-molding object improved remarkably and its manufacture method by covering a plastics base-material front face with the hardening film which consists of a specific three-tiered structure in detail.

[0002]

[Description of the Prior Art] Plastic material is used for the various use taking advantage of the features, such as shock resistance, lightweight nature, processability, and transparency. Especially the acrylic resin which is transparent plastics, polycarbonate resin, a styrene resin, etc. are broadly used as an alternative of glass. However, a front face tends to get damaged deficiently to abrasion-proof nature, and these resins have a fault -- a solvent is easy to be invaded.

[0003] Much proposals which improve surface hardness by covering the hardening film of a silicone system on the front face of plastics from the former in order to improve these faults have been made. For example, the covering constituent (JP,51-2736,A, JP,55-94971,A) which consists of a trihydroxy silane partial condensate and colloidal silica is mentioned, and these hardening coats give the abrasion resistance excellent in the plastics base material. However, in case heat hardening of these covering constituents is carried out, if impasto is carried out for the contraction accompanying formation of the bridge formation network structure, it will be easy to produce a crack, therefore they will usually be used by thickness about 6 micrometers or less, however, the influence of the surface hardness of a plastics base material comes out strongly according to coating thickness being thin, and enough -- it scratches and hardness is not obtained. Moreover, the constituent in which impasto is possible to some extent is indicated by three persons' suitable composition ratio in the hydrolysis condensate of tetrapod alkoxy silane, alkyltrialkoxysilane, and a dialkyl dialkoxysilane (JP,62-275170,A). Although a base material scratches and hardness is improved a little in this constituent, abrasion resistance is not obtained, but if a front face is ground by steel wool etc., it will get damaged easily. Moreover, the laminating of an urethane system paint film, the optical hardening film of a polyfunctional acrylate system resin, and the organopolysiloxane system heat-curing film is carried out one by one on a base material, and the method (JP,58-89359,A) of plastics scratching and improving hardness and wear-resistant both is proposed. It is necessary to stick an optical hardening layer and a siloxane layer at all, but to prepare a glue line between them further by this method, for the reason. It is not only complicated on operation, but [since optical hardening and heat curing are moreover combined,] in order to use an optical hardening film, it becomes a problem in respect of endurance, such as weatherability. Moreover, the primer constituent which contains the acrylic resin which has an alkoxy silyl machine on a base material as the improvement method of the surface hardness of a plastics base material is indicated (JP,5-78615,A). However, this method of consisting of two-layer structure has the inadequate adhesive property of a base material and a primer layer, and there is a problem also in endurance.

[0004]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to have abrasion resistance and the high surface hardness which scratches and is excellent in hardness, and offer the good plastic-molding object of endurance.

[0005]

[Means for Solving the Problem] That the fault of this plastic-molding object should be improved, wholeheartedly, as a result of research, this invention person found out that surface hardness, i.e., abrasion resistance, and the plastic-molding object which hardness is excellent by scratching and is further rich in adhesion endurance were acquired, and reached this invention by carrying out the laminating of the three-tiered structure which changes from a specific layer to a plastics base-material front face.

[0006] That is, this invention is the following formula (A) to a plastics base-material front face:

[0007]

[Formula 6]

$R_2-n-Si(OR_3)_{4-n} \dots (A)$

The inside R_2 of [] however a formula is the organic machine which has one or more bases chosen from the group which consists of the alkyl group of carbon numbers 1-4, a vinyl group or a meta-chestnut $ROKISHI$ machine, the amino group, an epoxy group, and a sulthydryl group. R_3 is the alkyl group of carbon numbers 1-4, and n is the integer of 0-2. [the hydrolyzate (portion) of the alkoxy silane come out of and shown, its partial condensate or 1-40% of the weight (weight criteria) by

dimethoxysilane, 3-glycidoxypolydimethoxysilane, 3-aminopropyl methyldiethoxysilane, etc. are mentioned. The hardening film obtained scratches, tetrapod alkoxy silane and methyl trialkoxy silane are desirable in respect of hardness, and methyl trimethoxy silane and methyl triethoxy silane are desirable in respect of economical efficiency and the endurance of a hardening film above all. These compounds are independent or can use two or more sorts collectively.

[0018] The alkoxy silane of the raw material which has not been understood as what a part or all of this alkoxy silane hydrolyzed, the condensate in which a part or all of this hydrolyzate carried out the condensation reaction, and this condensate an added water part condenses the hydrolyzate (portion) and its partial condensate of alkoxy silane, and these are obtained by so-called [carrying out a sol gel reaction.

[0019] The hydrolyzate (portion) and its partial condensate of the above-mentioned alkoxy silane Or it dilutes with a solvent, this alkoxy silane -- H₂O of alkoxy groups -- receiving -- usually -- the 0.5 to 10 time equivalent -- desirable -- the one to 5 time equivalent -- further -- desirable -- the water of the 1.5 to 3 time equivalent -- adding -- the bottom of existence of an acid catalyst -- a non-solvent -- A part or all of the thing to which a part or all hydrolyzed this alkoxy silane, and this hydrolyzate condenses, and these are obtained by [so-called] carrying out a sol gel reaction. The sol gel reaction mixture containing the hydrolyzate (portion) and its partial condensate of the alkoxy silane obtained in this way usually ripens, and is used. Although this digestion period does not generally have ***** since it is dependent on the kind and amount of the kind of alkoxy silane to be used and concentration, the amount of water, the kind of catalyst and an amount, and a diluent solvent, after it performs digestion for several days from several hours, it is usually used for the constituent for coating.

[0020] Here, as an acid catalyst to be used, organic acids, such as inorganic acids, such as a hydrochloric acid, a phosphoric acid, a sulfuric acid, a nitric acid, a nitrous acid, perchloric acid, and a sulfamic acid, a formic acid, an acetic acid, a propionic acid, butanoic acid, oxalic acid, a succinic acid, a maleic acid, a lactic acid, and p-toluenesulfonic acid, are mentioned, from the residual property at the time of making it the catalyst effect, the stability of a constituent, and a hardening film etc. -- desirable -- a hydrochloric acid and an acetic acid -- an acetic acid is mentioned especially preferably It is usually preferably used [as opposed to -- the concentration of 0.001 to 1 convention -- at an inorganic acid -- as opposed to -- this alkoxy silane -- at an organic acid] for this acid at 1 - 20 % of the weight 0.1 to 50% of the weight 0.0001 to 2 *****.

[0021] Addition in process, i.e., digestion, and all can use the solvent as a diluent preferably in the middle of the addition before the adding-water decomposition reaction of this alkoxy silane, or this reaction.

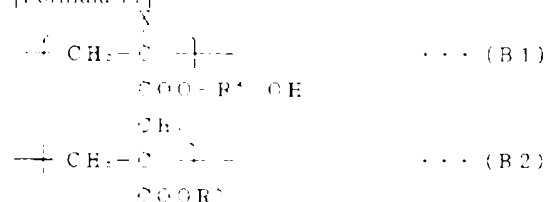
[0022] Furthermore, as the above-mentioned solvent, alcoholic system solvents, such as a methanol, ethanol, an isopropanol, n-butanol, a sec-butanol, a 4-methyl-2-pentanol, 2-ethoxyethanol, and 2-butoxy ethanol, are usually used. Two or more sorts of these solvents can be used together.

[0023] Moreover, as for the above-mentioned sol gel reaction mixture, it is desirable to make it pH 3.0-6.0 in respect of the stability.

[0024] The acrylic resin (1) used by the 1st layer of this invention is an acrylate system polymer which mainly consists of a repeating unit shown by the following formula (B1) and (B2) and which has a hydroxyl (meta).

[0025]

[Formula 11]



[0026] Here, the inside X of a formula is a hydrogen atom or a methyl group, and is R₄. It is the alkylene machine of carbon numbers 2-5, and is R₅. It is the alkyl group of carbon numbers 1-4, and p q is 1 - 99 - 50/50 in a mole ratio. Moreover, acrylate (meta) means methacrylate or acrylate.

[0027] The above-mentioned acrylic resin (1) is the copolymer of hydroxyl content (meta) acrylate and alkyl methacrylate, and can contain the other vinyl monomer component mentioned later. As this hydroxyl content (meta) acrylate For example, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate, 2-hydroxy-isopropyl methacrylate, 2-hydroxy-isopropyl acrylate, 4-hydroxy-butyl methacrylate, 4-hydroxy-butyl acrylate, 2-hydroxy-butyl methacrylate, 2-hydroxy-butyl acrylate, 2-hydroxy-2-methyl-propyl methacrylate, 2-hydroxy-2-methyl-propyl acrylate, 2-hydroxy-2-methyl-butyl methacrylate, 2-hydroxy-pentyl acrylate, 2-hydroxy-3-methyl-propyl methacrylate, 3-hydroxy-2 and 2-dimethyl propyl methacrylate etc. is mentioned. It is the point of the performance obtained and economical efficiency, and 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl methacrylate, and 2-hydroxypropyl acrylate are especially desirable, these compounds are independent -- or two or more sorts can be used collectively. Moreover, as alkyl methacrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, etc. are mentioned. It is the point of the performance obtained and especially methyl methacrylate and ethyl methacrylate are desirable. It milks -- it falls, and -- it is easy to carry out micro phase separation of the compatibility with the above-mentioned sol gel solution, and [as a result and is not desirable although it will think for a hydrophobic property to increase if the carbon number of the alkyl group of this alkyl methacrylate becomes five or more, these compounds are independent -- or two or more sorts can be used collectively.

[0028] When this acrylic resin (I) sets to p and q the mole ratio of the acrylate repeating unit which has the hydroxyl expressed with the above-mentioned formula (B1) (meta), and the alkyl methacrylate repeating unit expressed with the above-mentioned formula (B-2), respectively, p/q is 1 - 99 - 50/50, and a polymer that mainly consists of 5 - 95 - 40/60 preferably in a mole ratio. If there are few hydroxyls than one-mol %, sufficient endurance will not be acquired, but if [than 50 mol %] more, adhesion with a base material may fall.

[0029] moreover, the purpose which raises [endurance] disadvantage ***** an adhesive property, solubility, [the original performance to this acrylic resin -- the above-mentioned (meta) acrylate polymer -- receiving -- less than 30 mol % -- desirable -- less than 15 mol % -- it can come out comparatively and other vinyl monomers can be added as a copolymerization component

[0030] As this vinyl monomer, styrene, vinyl acetate, acrylonitrile, a methacrylonitrile, an acrylic acid, a methacrylic acid, methyl acrylate, ethyl acrylate, 2-ethylhexyl methacrylate, etc. are mentioned.

[0031] Although this acrylic resin is obtained by carrying out a polymerization by arbitrary well-known methods using the acrylate and alkyl methacrylate which have the above-mentioned hydroxyl (meta), it is the point which does not contain random copolymerization nature and an ionicity impurity, and its radical copolymerization method in the inside of an inactive solvent is desirable.

[0032] As this polymerization solvent, alcohols, such as ester, such as ether, such as ketones, such as hydrocarbons, such as benzene, toluene, a xylene, a cyclohexane, and a hexane, an acetone, a methyl ethyl ketone, and a methyl isobutyl ketone, 1, 2-dimethoxyethane, 1, 3-dioxane, and a tetrahydrofuran, ethyl acetate, butyl acetate, and ethoxy ethyl acetate, a methanol, ethanol, an isopropanol, and n-butanol, are mentioned. These solvents may use two or more sorts together.

[0033] Although polymerization temperature and polymerization time do not generally have ***** since it is dependent on the initiator to be used, they are usually 4 - 10 hours preferably at 60-80 degrees C 50-100 degrees C for 2 to 24 hours that what is necessary is just to use suitably a radical initiator well-known as a polymerization initiator.

[0034] The molecular weight of the acrylic resin of the 1st layer of this invention is 50,000 or more preferably 20,000 or more in weight average molecular weight at least, in order to fully demonstrate the performance as the 1st layer.

[0035] The 1st layer in this invention is formed by using this as a constituent for coating, after mixing the sol gel reaction mixture containing the hydrolyzate (portion), its partial condensate, or these ***** of the above-mentioned alkoxy silane, and the solution which dissolved the above-mentioned acrylic resin (I) and leaving it under ordinary temperature preferably for several hours or more. By carrying out ordinary temperature neglect for several hours or more, this constituent for coating is transparent, and a uniform hardening film without a crack is obtained. As this reason, if it is left in this way, a hydrolyzate (portion), its partial condensate or such mixture (sol gel reactant), and the hydroxyl of the side chain of this acrylic resin react partially, or hydrogen bond will be carried out and it will be presumed that micro equalization is carried out etc.

[0036] The former is [the 5 - 35-% of the weight (calculation as However, $R_2nSiO(4-n) - 2$) latter of the mixed quantitative ratio of the hydrolyzate (portion) of the above-mentioned alkoxy silane, its partial condensate or such mixture (sol gel reactant), and acrylic resin (I)] 95 - 65 % of the weight preferably 99 to 60% of the weight one to 40% of the weight. Adhesion with a plastics base material may fall that it will be easy to produce a crack on a hardening film if there are too many amounts of a sol gel reactant, and if too few, the endurance of a hardening film, especially water resistance will fall.

[0037] What is necessary is to dissolve both the components of the sol gel reaction mixture containing this sol gel reaction mixture, after mixture and this acrylic resin, and sol gel reaction mixture, and just not to spoil the stability of a sol gel reactant as a solvent which dissolves this acrylic resin. Specifically 1-ethanol, an isopropanol, n-butanol, a sec-butanol, The 2-ethoxyethanol, a 4-methyl-2-pentanol, 2-butoxy ethanol, Alcohols, such as diacetone alcohol, an acetone, a methyl ethyl ketone, Methyl isopropyl ketone, a methyl isobutyl ketone, a methyl n-amyl ketone, Ketones, such as a cyclohexanone, a diisopropyl ether, a tetrahydrofuran, 1, 4-dioxane, 1, 3-dioxolane, 1, 2-dimethoxyethane, Ether, such as 1 and 2 diethoxy ethane, benzene, toluene, a xylene, Ester, such as hydrocarbons, such as a cyclohexane and n-hexane, ethyl acetate, butyl acetate, 2-ethoxy ethyl acetate, 2-butoxy ethyl acetate, and ethyl butyrate, an acetonitrile, a nitromethane, etc. are mentioned. Especially, a ketone system solvent is desirable and a methyl ethyl ketone and a methyl isobutyl ketone are especially desirable. Moreover, these solvents can use two or more sorts together.

[0038] It is usually 3 - 30 % of the weight preferably one to 40% of the weight, and the whole quantity may originate a solid-content content in this sol Ringer's injection and an acrylic resin solution, or the solvent as a residue may newly add the content of what the above-mentioned constituent for coating used for forming the 1st layer of this invention becomes from the hardened material obtained by the sol gel reaction and acrylic resin (I) (henceforth a solid content). It is chosen out of the solvent of the above-mentioned acrylic resin as this solvent. Moreover, the thing of the total amount of solvents chosen from the alcoholic desirable system solvent of the above about 20% of the weight about 10% of the weight or more at least is desirable

[0039] this constituent for coating -- as a curing catalyst -- usually -- quarternary ammonium salt, such as alkali-metal salts, such as lithium salt of aliphatic carboxylic acids, such as a formic acid, an acetic acid, a propionic acid, butanoic acid, a lactic acid, a tartaric acid, and a succinic acid, sodium salt, and potassium salt, a benzyl trimethylammonium salt, a tetramethylammonium salt, and a tetraethylammonium salt, -- sodium acetate, potassium acetate, acetic-acid tetramethylammonium, and benzyl-acetate trimethylammonium are contained preferably.

[0040] Although the amount of a curing catalyst does not generally have ***** since it changes with a curing temperature and the setting times, it is usually desirable to add in 0.1 - 15 weight section to this alkoxy silane 100 weight section (calculation as [However] weight criteria by $R_2nSiO(4-n) - 2$ conversions).

[0041] moreover, this constituent for coating -- endurance, such as water resistance, -- and it may scratch and melamine resin may be contained for the purpose of improvement in hardness etc. As this melamine resin, the thing by which some or all of a methylol machine of a hexa methylol melamine was methyl-ether-ized, or the thing by which some or all of this methylol machine was butyl-ether-ized is mentioned, those monomers or oligomer various kinds is marketed, and all can be used preferably. For example, the Cymel resin of Mitsui SAIITEKKU, Inc. and the you van resin of Mitsui Toatsu Chemicals, Inc. are mentioned. This melamine resin is preferably used below in 50 weight sections below the 100 weight sections to the above-mentioned acrylic resin (I) 100 weight section.

[0042] The making low temperature and a short time harden this melamine resin comparatively, purpose, an acid catalyst can be used. As this acid catalyst, a benzenesulfonic acid, p-toluenesulfonic acid, methansulfonic acid, a phthalic acid, a maleic acid, an itaconic acid, a succinic acid, a citric acid, an acetic acid, a propionic acid, a phosphoric acid, phosphorous acid, phenylphosphonic acid, a nitric acid, a hydrochloric acid, a sulfuric acid, a sulfamic acid, etc. are mentioned, and these acids are suitably chosen according to the purpose. This acid is usually preferably added below in 5 weight sections below 20 weight sections to the melamine resin 100 weight section.

[0043] Moreover, the above-mentioned constituent for coating can contain a light stabilizer and an ultraviolet ray absorbent, in order to improve the weatherability of a plastics base material. Moreover, these ** can also be used together.

[0044] As a light stabilizer, for example Screw (2, 2, 6, and 6-tetramethyl-4-piperidyl) carbonate, Screw (2, 2, 6, and 6-tetramethyl-4-piperidyl) succinate, Screw (2, 2, 6, and 6-tetramethyl-4-piperidyl) sebacate, 4-benzoyloxy - 2, 2, 6, and 6-tetramethylpiperidine, 4-hexanoyloxy - 2, 2, 6, and 6-tetramethylpiperidine, Oxy-[4-octanoyl] - 2, 2, 6, and 6-tetramethylpiperidine, Screw (2, 2, 6, and 6-tetramethyl-4-piperidyl) diphenylmethane - p and p'-dicarbamate, Screw (2, 2, 6, and 6-tetramethyl-4-piperidyl) benzene -1, 3-disulfio NE10, Hindered amine, such as screw (2, 2, 6, and 6-tetramethyl-4-piperidyl) phenyl phosphite Nickel screw (octyl phenyl) sulfide, [2 and 2'-thio screw (4-tert-octyl phenolate)] N-butylamine nickel, [2 and 2'-thio screw (4-tert-octyl phenolate)] triethanolamine nickel, Nickel complex - 3 Five - Nickel complexes, such as G tert-butyl-4-hydroxy benzyl phosphoric-acid monochrome ethylate and nickel dibutylldithiocarbamate, are mentioned, these ** are independent -- it is -- carrying out -- two or more sorts may be used together and it is usually preferably used below in 20 weight sections below 50 weight sections to the acrylic resin 100 weight section.

[0045] As an ultraviolet ray absorbent, for example 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-octoxybenzophenone, 2, 4-dihydroxy benzophenone, Benzophenones, such as 2 and 2'-dihydroxy-4-methoxybenzophenone 2-(5'-methyl-2'-hydroxyphenyl) benzotriazol, A 2-[2'-hydroxy-3', 5'-screw (alpha, alpha dimethyl benzyl) phenyl]-2H-benzotriazol, 2-(3', 5'-G tert-butyl-2'-hydroxyphenyl) benzotriazol, A 2-(3'-tert-butyl-5'-methyl-2'-hydroxyphenyl)-5-chloro benzotriazol, 2-(2'-hydroxy-5'-tert-octyl phenyl) benzotriazol, A 2-(3', 5'-G tert-butyl-2'-hydroxyphenyl)-5-chloro benzotriazol, Benzotriazols, such as 2-(3', 5'-G tert-amyl-2'-hydroxyphenyl) benzotriazol Cyanoacrylate, such as the ethyl-2-cyano -3, 3-diphenyl acrylate, the 2-ethylhexyl-2-cyano -3, and 3-diphenyl acrylate A phenyl SARISHI rate, a p-tert-butylphenyl SARISHI rate, Benzylidene malonate, such as SARISHI rates, such as p-octyl phenyl SARISHI rate, diethyl p-methoxy benzylidene malonate, and screw (2-ethylhexyl) benzylidene malonate, is mentioned, these ** are independent -- it is -- carrying out -- two or more sorts may be used together and it is usually preferably used below in 50 weight sections below the 100 weight sections to this acrylic resin 100 weight section.

[0046] The constituent for coating for the 1st layer in this invention is applied on a plastics base material by methods usually used, such as a DIP coat, a spray coat, a flow coat, a roll coat, a bar coat, and a spin coat, and can be suitably chosen with the configuration of this base material etc. dryness removal of a solvent should usually do the base material to which this constituent was applied under the temperature below the heat deflection temperature of this base material from ordinary temperature -- subsequently -- about 40- the complex film of the organopolysiloxane and acrylic resin which are the 1st layer of this invention is formed by carrying out heat hardening at the temperature of about 140 degrees C for - about 4 hours during about 10 minutes.

[0047] A part or all of heat hardening can serve as the heat hardening of the 3rd layer in the below-mentioned 2nd layer row by which a laminating is carried out on the 1st layer.

[0048] 0.1-10 micrometers of thickness of the 1st layer are usually 1-5 micrometers preferably that what is necessary is just thickness required to fully paste up a plastics base material and the 2nd layer or subsequent ones in this invention, and able to hold the initial complement of the above-mentioned weatherproof improvement agent.

[0049] When the complex film which consists of the above-mentioned organopolysiloxane and acrylic resin (I) forms the 1st layer, the adhesion of the 2nd layer and plastics base material which are mentioned later becomes good, and the plastic-molding object excellent in endurance can be acquired.

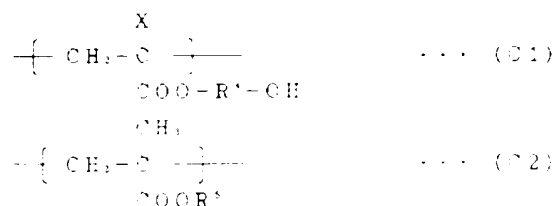
[0050] The 2nd layer in this invention is a thin film layer obtained by heat-hardening the hydrolyzate (portion) of alkoxysilane, its partial condensate or such mixture, the mixture of the acrylic resin which has a specific functional group, or a reactant.

[0051] The same thing as what is used for the hydrolyzate (portion), its partial condensate, or such mixture of the alkoxysilane used by the 2nd layer in this invention forming the 1st above-mentioned layer can be used.

[0052] The acrylic resin (II) which has the hydroxyl used by the 2nd layer of this invention is an acrylate system polymer which mainly consists of the following formula (C 1) and (C 2) a repeating unit shown in meta)

[0053]

[Formula 12]



[0054] Here, the inside X of a formula is a hydrogen atom or a methyl group, and is R4. It is the alkylene machine of carbon numbers 2-5, and is R5. It is the alkyl group of carbon numbers 1-4. When molar quantity of the above-mentioned formula (C1) and (C2) the repeat unit expressed is set to r and s, respectively, r/s is 1/99 - 100/0 in a mole ratio. Moreover, acrylate (meta) means methacrylate or acrylate.

[0055] This acrylic resin (II) is the homopolymer of the acrylate which has a hydroxyl (meta), or the copolymer of this hydroxyl content (meta) acrylate and alkyl methacrylate, and can contain the other vinyl monomer component mentioned later. As this hydroxyl content (meta) acrylate For example, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate, 2-hydroxy-isopropyl methacrylate, 2-hydroxy-isopropyl acrylate, 4-hydroxy butyl methacrylate, 4-hydroxy butyl acrylate, 2-hydroxy butyl methacrylate, 2-hydroxy butyl acrylate, 2-hydroxy-2-methyl-propyl methacrylate, 2-hydroxy-2-methyl-propyl acrylate, 2-hydroxy-2-methyl-butyl methacrylate, 2-hydroxy-pentyl acrylate, 2-hydroxy-3-methyl-propyl methacrylate, 3-hydroxy - 2 and 2-dimethyl propyl methacrylate etc. is mentioned. It is the point of the performance obtained and economical efficiency, and 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl methacrylate, and 2-hydroxypropyl acrylate are especially desirable, these compounds are independent -- or two or more sorts can be used collectively. Moreover, as alkyl methacrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, teri-butyl methacrylate, etc. are mentioned. It is the point of the performance obtained and especially methyl methacrylate and ethyl methacrylate are desirable. It milks [it falls, and] it is easy to carry out micro phase separation of the compatibility with the above-mentioned sol gel solution, and] as a result and is not desirable although it will think for a hydrophobic property to increase if the carbon number of the alkyl group of this alkyl methacrylate becomes five or more, these compounds are independent -- or two or more sorts can be used collectively.

[0056] The mole ratios (r/s) of the acrylate repeating unit and alkyl methacrylate repeating unit in which the above-mentioned acrylic resin (II) has a hydroxyl (meta) are 1/99 - 100/0, and a polymer that mainly consists of 5/95 - 100/0 preferably, enough, when there are few hydroxyls than one-mol % -- it scratches and hardness is not obtained.

[0057] moreover, the purpose which raises [endurance -- disadvantage ***** an adhesive property, solubility,] the original performance to this acrylic resin -- the above-mentioned (meta) acrylate polymer -- receiving -- less than 30 mol % -- desirable -- less than 15 mol % -- it can come out comparatively and other vinyl monomers can be added as a copolymerization component.

[0058] As this vinyl monomer, styrene, vinyl acetate, acrylonitrile, a methacrylonitrile, an acrylic acid, a methacrylic acid, methyl acrylate, ethyl acrylate, 2-ethylhexyl methacrylate, etc. are mentioned.

[0059] Although this acrylic resin (II) is obtained by carrying out a polymerization by arbitrary well-known methods using the acrylate and alkyl methacrylate which have the above-mentioned hydroxyl (meta), it is the point which does not contain random copolymerization nature and an ionicity impurity, and its radical copolymerization method in the inside of an inactive solvent is desirable.

[0060] As this polymerization solvent, alcohols, such as ester, such as ether, such as ketones, such as hydrocarbons, such as benzene, toluene, a xylene, a cyclohexane, and a hexane, an acetone, a methyl ethyl ketone, and a methyl isobutyl ketone, 1, 2-dimethoxyethane, 1, 3-dioxane, and a tetrahydrofuran, ethyl acetate, butyl acetate, and ethoxy ethyl acetate, a methanol, ethanol, an isopropanol, and n-butanol, are mentioned. These solvents may use two or more sorts together.

[0061] Although polymerization temperature and polymerization time do not generally have ***** since it is dependent on the initiator to be used, they are usually 4 - 10 hours preferably at 60-80 degrees C, 50-100 degrees C for 2 to 24 hours that what is necessary is just to use suitably a radical initiator well-known as a polymerization initiator.

[0062] the molecular weight of the above-mentioned acrylic resin (II) -- weight average molecular weight -- 20,000-600,000 -- it is the range of 40,000-400,000 preferably. The stability of the constituent for coating which will be later mentioned if a low, paint film nature, and the membranous flexibility acquired are lower than 20,000, it is easy to produce a crack and molecular weight is higher than 600,000 falls.

[0063] The 2nd layer in this invention is formed by using this as a constituent for coating, after mixing the sol gel reaction mixture containing the hydrolyzate (portion), its partial condensate, or these ***** of the above-mentioned alkoxy silane, and the solution which dissolved the above-mentioned acrylic resin (II) and leaving it under ordinary temperature preferably for several hours or more. By carrying out ordinary temperature neglect for several hours or more, this constituent for coating is transparent, and a uniform hardening film without a crack is obtained. As this reason, a sol gel reactant and the hydroxyl of the side chain of acrylic resin react partially during [this] the neglect, or hydrogen bond is carried out, and it is presumed that micro equalization is carried out etc.

[0064] The former is [the latter of the mixed quantitative ratio of the hydrolyzate (portion), its partial condensate or such mixture, and acrylic resin (II) of the above-mentioned alkoxy silane] 50 - 20% of the weight preferably, 60 to 10% of the weight, 40 to 90% of the weight, 50 to 80% of the weight calculation as [However,] weight criteria by $R_2nSiO_{(4-n)/2}$.

conversions). If there are too many amounts of a sol gel reactant, it will be easy to produce a crack on a hardening film, if too few, the endurance of a hardening film, especially water resistance will fall, and a hardening film scratches, and hardness runs short.

[0065] What is necessary is to dissolve sol gel reaction mixture and both the components after mixture, and just not to spoil the stability of a sol gel reactant as a solvent of this acrylic resin. Specifically Ethanol, an isopropanol, n-butanol, a sec-butanol. The 2-ethoxyethanol, a 4-methyl-2-pentanol, 2-butoxy ethanol. Alcohols, such as diacetone alcohol, an acetone, a methyl ethyl ketone, Methyl isopropyl ketone, a methyl isobutyl ketone, a methyl n-amyl ketone. Ketones, such as a cyclohexanone, a diisopropyl ether, a tetrahydrofuran, 1, 4-dioxane, 1, 3-dioxolane, 1, 2-dimethoxyethane. Ether, such as 1 and 2 diethoxy ethane, benzene, toluene, a xylene. Ester, such as hydrocarbons, such as a cyclohexane and n-hexane, ethyl acetate, butyl acetate, 2-ethoxy ethyl acetate, 2-butoxy ethyl acetate, and ethyl butyrate, an acetonitrile, a nitromethane, etc., are mentioned. Especially, a ketone system solvent is desirable and a methyl ethyl ketone and a methyl isobutyl ketone are especially desirable. Moreover, these solvents can use two or more sorts together.

[0066] The above-mentioned solution which consists of acrylic resin and a solvent can make the alkoxy silyl machine of the side chain of this acrylic resin understand an added water part beforehand (portion), as water and the acid catalyst were added and described above in this solution, before mixing with the above-mentioned sol gel reaction mixture.

[0067] Usually, three to 50% of the weight, it is 5 - 35 % of the weight preferably, and the whole quantity may originate in this sol Ringer's injection and an acrylic resin solution, or the solvent as a residue may newly add the content of what the constituent for coating used for forming the 2nd layer of this invention becomes from the hardened material obtained by the sol gel reaction and the acrylic resin (II) which has the above-mentioned specific functional group (henceforth a solid content). It is chosen out of the solvent of the above-mentioned acrylic resin as this solvent. Moreover, even if there are few total amounts of solvents, it is chosen out of the alcoholic desirable system solvent of the above about 20% of the weight about 10% of the weight or more.

[0068] this constituent for coating -- as a curing catalyst -- usually -- quarternary ammonium salt, such as alkali-metal salts, such as lithium salt of aliphatic carboxylic acids, such as a formic acid, an acetic acid, a propionic acid, butanoic acid, a lactic acid, a tartaric acid, and a succinic acid, sodium salt, and potassium salt, a benzyl trimethylammonium salt, a tetramethylammonium salt, and a tetraethylammonium salt, -- sodium acetate, potassium acetate, acetic-acid tetramethylammonium, and benzyl-acetate trimethylammonium are contained preferably.

[0069] Although the amount of a curing catalyst does not generally have ***** since it changes with a curing temperature and the setting times, it is usually desirable to add in 0.1 - 15 weight section to this alkoxy silane 100 weight section (calculation as $[R_2nSiO(4-n)] \cdot 2$).

[0070] moreover, this constituent for coating -- endurance, such as water resistance, -- and it may scratch and melamine resin may be contained for the purpose of improvement in hardness etc. As this melamine resin, the thing by which some or all of a methylol machine of a hexa methylol melamine was methyl-ether-ized, or the thing to which some or all of this methylol machine was carried out in the butyl ether is mentioned, those monomers or oligomer various kinds is marketed, and all can be used preferably. For example, the Cymel resin of Mitsui SAIHKKU, Inc. and the you van resin of Mitsui Toatsu Chemicals, Inc. are mentioned. This melamine resin is usually preferably used below in 50 weight sections below the 100 weight sections to the above-mentioned acrylic resin 100 weight section. Superfluous addition of this melamine may make the above-mentioned constituent gel.

[0071] The making low temperature and a short time harden this melamine resin comparatively purpose, an acid catalyst can be used. As this acid catalyst, a benzenesulfonic acid, p-toluenesulfonic acid, methansulfonic acid, a phthalic acid, a maleic acid, an itaconic acid, a succinic acid, a citric acid, an acetic acid, a propionic acid, a phosphoric acid, phosphorous acid, phenylphosphonic acid, a nitric acid, a hydrochloric acid, a sulfuric acid, a sulfamic acid, etc., are mentioned, and these acids are suitably chosen according to the purpose. This acid is usually preferably added below in 5 weight sections below 20 weight sections to the melamine resin 100 section.

[0072] Moreover, in this constituent for the 2nd layer, additives which were mentioned above, such as a light stabilizer and an ultraviolet ray absorbent, can be contained in the amount which does not spoil the paint film performance of the 2nd layer in order to improve the weatherability of a plastics base material further. Usually, this ** can also use two or more sorts together, and they can be preferably used for it below by 10 weight sections below 20 weight sections in the additive sum total to the solid-content 100 weight section of this constituent.

[0073] The constituent for coating for the 2nd layer in this invention is applied on the 1st layer formed on the aforementioned plastics base material. As the method of application, methods usually used, such as a DIP coat, a spray coat, a flow coat, a roller coat, a bar coat, and a spin coat, are used, and it can choose suitably with the configuration of this Plastic solid etc. The complex film of organopolysiloxane and acrylic resin which is the 2nd layer of this invention is formed by usually making dryness removal of a solvent under the temperature below the heat deflection temperature of this base material from ordinary temperature, and subsequently carrying out heat hardening of the applied Plastic solid at the temperature of 40-140 degrees C for - 4 hours during 10 minutes.

[0074] A part or all of heat hardening can serve as the heat hardening of the 3rd layer by which a laminating is carried out on the 2nd layer.

[0075] the thickness of the 2nd layer needs -- although it scratches and changes with hardness -- usually -- 5-80-micrometer 3-100 micrometers are 8-50 micrometers still more preferably preferably. It will scratch, if thickness is smaller than 3 micrometers, and the improvement effect of hardness is not acquired, but if larger than 100 micrometers, a crack will tend to

produce it.

[0076] The 3rd layer is formed using the coating constituent which consists of a solvent, an acid, and a small amount of curing catalyst including the hydrolyzate (portion), its partial condensate, or such mixture of the alkoxy silane shown by the following formula (E) as a substantial solid content.

{0077}

[Formula 13]

$$\text{R}_9\text{-x-Si(OR}_{10}\text{)}_{4-x}\dots\text{(E)}$$

Here, it is the inside R9 of a formula. It is the alkyl group of the carbon numbers 1-3 replaced by the alkyl group of carbon numbers 1-4, the vinyl group or the meta-chestnut ROKISHI machine, the amino group, and one or more bases chosen from the group which consists of a glycidoxymachine, R10 is the alkyl group of carbon numbers 1-4, and x is the integer of 0-2.

The above-mentioned alkoxy silane can use both a tetrapod TORI and a dialkoxy silane. As this tetrapod alkoxy silane, for example, a tetramethoxy silane, a tetrapod ethoxy silane, tetrapod isopropoxysilane, tetrapod n-butoxysilane, etc. are mentioned. Above all, a tetramethoxy silane and a tetrapod ethoxy silane are desirable economical efficiency and in respect of reactivity. As trialkoxysilane, for example Methyl trimethoxysilane, Methyl triethoxysilane, a methyl triisopropoxy silane, MECHUR TORI n-butoxysilane, Ethyl trimethoxysilane, ethyltriethoxysilane, an ethyl triisopropoxy silane,

[0078] This alkoxy silane mainly has a desirable bird clapper on the performance of the paint film obtained from the tetrapod alkoxy silane not more than 40 mol %, and the trialkoxy silane beyond 60 mol %. Although the abrasion resistance of the paint film obtained by using tetrapod alkoxy silane improves, if more tetrapod alkoxy silane than 40-mol % is used, this paint film will become comparatively weak and a crack will become easy to produce it.

[0079] In addition, the hydrolyzate (portion) and its partial condensate of the above-mentioned alkoxy silane are the thing and homonymy which are obtained by 1 in said 1st layer and the 2nd layer—so-called 1 carrying out a sol-gel reaction.

[0080] As for the 3rd layer, it is also desirable to contain colloidal silica. That is, it is formed using the coating constituent which consists of a solvent, an acid, and a small amount of curing catalyst including the hydrolyzate (portion), its partial condensate or such mixture, and colloidal silica of the trialkoxysilane (it corresponds to $x = 1$ in the above-mentioned formula (I)) shown by the following formula (D) as a substantial solid content.

[0081]

[Formula 1.4]

$$\text{R7-Si3 (OR8)}_{\text{m}} \text{ (12)}$$

Here, it is the inside R7 of a formula. It is the alkyl group of the carbon numbers 1-3 replaced by the alkyl group of carbon numbers 1-4, the vinyl group or the meta-chestnut ROKISHI machine, the amino group, and one or more bases chosen from the group which consists of a glycidooxy machine, and is R8. It is the alkyl group of carbon numbers 1-4.

[0082] As trialkoxysilane expressed with the above-mentioned formula (D) For example, methyl trimethoxysilane, methyl triethoxysilane, a methyl triisopropoxy silane, MECHIRUTORI n-butoxysilane, ethyl trimethoxysilane, ethyl triethoxysilane, An ethyl triisopropoxy silane, propyltrimethoxysilane, butyltrimethoxysilane, Vinyltrimethoxysilane, vinyltriethoxysilane, 3-methacryloxy propyl trimethoxysilane, 3-methacryloxypropyl triethoxysilane, meta-chestnut ROKISHI methyl trimethoxysilane, Meta-KI RIROKISHI methyl triethoxysilane, 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, etc. are mentioned.

[0083] Moreover, it is desirable among trialkoxysilane at least 70% of the weight of that it is methyl trialkoxysilane in respect of the abrasion resistance of the hardening film obtained, it is more desirable that the whole quantity of this trialkoxysilane is methyl trialkoxysilane, and methyl trimetoxysilane and methyl triethoxysilane are still more desirable especially. These compounds are independent, or can be combined two or more sorts and can be used. Moreover, it is also desirable to carry out little addition of the above-mentioned trialkoxysilane other than methyl trialkoxysilane for the purpose of other functional grants.

[0084] Although the aqueosity distribution liquid or low-grade fatty alcohol distribution liquid with which 5-100nm of the particle size is 10-50nm preferably, and colloidal silica is usually contained ten to 50% of the weight as colloidal silica is used, the thing of aqueosity distribution liquid is used preferably. Such colloidal silica is marketed with tradenames, such as RU DOCKI SL (Ludox) of Nissan Chemical Industries, KALAROIDO of catalyst Chemicals industry, Oscar, and U. S. Du Pont, and NARI KOOL (Nalcoag) of U.S. Nalco Chemical.

[0085] Although the mixed rate of the hydrolyzate (portion), its partial condensate or such mixture, and colloidal silica of trialkoxysilane is decided from points, such as existence of the stability of the coating constituent to be used, the transparency of the hardening film obtained, abrasion resistance, and crack initiation the inside of the 3rd layer finally formed -- the hydrolyzate (portion) of this trialkoxysilane, its partial condensate or 90 ~ 30 % of the weight (calculation as 1. However, 1

weight criteria by R7 SiO₃ 2 conversion) of such mixture, and colloidal silica -- 10 - 70 % of the weight -- it is made to become comparatively Moreover, the hydrolyzate poured (portion), its partial condensate or such mixture, and colloidal silica are preferably contained in 15 - 30% of the weight of the range ten to 50% of the weight in a coating constituent as a substantial solid content.

[0086] the hydrolyzate (portion) and its partial condensate of the alkoxy silane expressed with the above-mentioned formula (E) (and (D)) -- 1:1 eq of alkoxy groups of this alkoxy silane -- receiving -- usually -- the 1 - 10 time equivalent -- desirable -- the 1.5 - 7 time equivalent -- further -- desirable -- the water of the 2 - 4 time equivalent -- adding -- the bottom of existence of an acid catalyst -- a non-solvent -- or it can obtain by making it react to the bottom of dilution with a solvent Although the water of sufficient amount usually needed at the adding-water decomposition reaction of trialkoxy silane and a partial condensation reaction is contained in the colloidal silica aqueous distribution liquid to be used in the case of the trialkoxy silane of the above-mentioned formula (D), as long as it requires, you may add water further. In this way, in water - alcoholic system acid medium, if Si-OH generates by hydrolysis, a hydroxyl will condense the alkoxy silane (portion) hydrolyzate obtained, its partial condensate, or such mixture, and they will form Si-O-Si combination. However, condensation is not perfect and is partial, and this condensate holds most quantity of a Si-OH basis, and, thereby, is dissolving it into water - alcoholic solvent. [0087] The sol gel reaction mixture containing the hydrolyzate (portion) of this alkoxy silane, its partial condensate, or such mixture usually ripens, and is used. Although there is no ***** generally since it is dependent on the kind and amount of the kind of alkoxy silane to be used and concentration, the amount of water, the kind of catalyst and an amount, and a diluent solvent, the digestion period in this case is usually used as a constituent for coating, after making it ripe for several days from several hours.

[0088] It is required for the hydrolyzate (portion), its above-mentioned partial condensate, or such above-mentioned mixture of alkoxy silane to dissolve stably as a solvent used for this coating constituent, and, for that, it is desirable for 50 % of the weight or more to be alcohol preferably at least 20% of the weight or more. As this alcohol, a methanol, ethanol, an isopropanol, n-butanol, a sec-butanol, the 2-ethoxy ethanol, a 4-methyl-2-pentanol, 2-butoxy ethanol, etc. are mentioned, for example, the alcohol of the low boiling point of carbon numbers 1-4 is desirable, and an isopropanol is desirable especially in respect of solubility, stability, and coating nature. In this solvent, the low-grade fatty alcohol as the water for the excess which does not participate in this adding-water decomposition reaction among the water as a dispersion medium of the low-grade fatty alcohol accompanying hydrolysis of the above-mentioned trialkoxy silane and colloidal silica, or a dispersion medium of colloidal silica is also contained. As other solvents, to mix with water alcohol is required, for example, ester, such as ether, such as ketones [], such as an acetone a methyl ethyl ketone, and a methyl isobutyl ketone, [], tetrahydrofuran, 1, 4-dioxane, [], and 2-dimethoxyethane, ethyl acetate, and ethoxy ethyl acetate, is mentioned.

[0089] It is required for the hydrolyzate (portion), its above-mentioned partial condensate, or such above-mentioned mixture of alkoxy silane to dissolve stably as a solvent used for this coating constituent, and, for that, it is desirable for 50 % of the weight or more to be alcohol preferably at least 20% of the weight or more. As this alcohol, a methanol, ethanol, an isopropanol, n-butanol, a sec-butanol, the 2-ethoxy ethanol, a 4-methyl-2-pentanol, 2-butoxy ethanol, etc. are mentioned, for example, the alcohol of the low boiling point of carbon numbers 1-4 is desirable, and an isopropanol is desirable especially in respect of solubility, stability, and coating nature. In this solvent, the low-grade fatty alcohol accompanying hydrolysis of the above-mentioned alkoxy silane is also contained. As other solvents, to mix with water alcohol is required, for example, ester, such as ether, such as ketones [], such as an acetone a methyl ethyl ketone, and a methyl isobutyl ketone, [], tetrahydrofuran, 1, 4-dioxane, 1, and 2-dimethoxyethane, ethyl acetate, and ethoxy ethyl acetate, is mentioned.

[0090] When this coating constituent contains a suitable acid, it is required 3.0-6.0, and to adjust pH to 4.0-5.5 preferably. Thereby, while promoting the adding-water decomposition reaction of the above-mentioned alkoxy silane, and a partial condensation reaction, gelling in ordinary temperature can be prevented and preservation stability can be increased. It may add to alkoxy silane beforehand or this acid may be added after hydrolysis of this alkoxy silane. Moreover, this addition can also be divided into 1 time or 2 times or more. As an acid used, organic acids, such as inorganic acids, such as a hydrochloric acid, a phosphoric acid, a sulfuric acid, a nitric acid, a nitrous acid, perchloric acid, and a sulfamic acid, a formic acid, an acetic acid, a propionic acid, butanoic acid, oxalic acid, a succinic acid, a maleic acid, a lactic acid, and p-toluenesulfonic acid, are mentioned, for example, and especially a hydrochloric acid or an acetic acid is desirable. Although this acid changes with the acidity etc., it is usually added at 2 or less % of the weight to this constituent.

[0091] Furthermore, the catalyst for promoting heat curing contains in this coating constituent. The thing same as this catalyst as said curing catalyst of the 2nd layer can be used. Sodium acetate, potassium acetate, benzyl-acetate trimethylammonium, and acetic-acid tetramethyl AMMONIUM are especially desirable. Although an addition changes with hardening conditions, it is 0.05 - 2 % of the weight preferably 0.01 to 5 % of the weight to this constituent. If there are few additions than 0.01 % of the weight, sufficient cure rate will not be obtained, but if [] than 5 % of the weight [] more, preservation stability will fall or precipitate will be produced.

[0092] The above-mentioned coating constituent for the 3rd layer in this invention is applied to up to the 2nd aforementioned layer, and the 3rd layer is formed by heating. In order to apply this coating constituent, methods usually used, such as a DIP coat, a spray coat, a flow coat, a roll coat, a bar coat, and a spin coat, are used, and it can choose suitably with the configuration of this Plastic solid etc. the applied Plastic solid -- usually -- the bottom, of the temperature below the heat deflection temperature of ordinary temperature to this base material -- evaporation removal of a solvent -- it carries out. Subsequently, at the temperature of 50-150 degrees C., the silanol which carries out heat hardening for - 4 hours during 10 minutes and which remains in this process is condensed, and the thin film of the abrasion resistance of the 3rd layer in this

invention and solvent resistance pastes up firmly through the 1st layer and the 2nd layer on a plastic-molding object.

[0093] A part or all of this heat-hardening operation can serve as the heat hardening of the 2nd layer, as described above.

[0094] 2-8 micrometers of thickness of the 3rd layer are 1-10 micrometers usually 3-7 micrometers still more preferably. If thickness is smaller than 1 micrometer, sufficient abrasion resistance will not be obtained, but if larger than 10 micrometers, it will be easy to generate a crack.

[0095] A well-known leveling agent can be added and used for this constituent in order to improve the 1st layer of this invention, the 2nd layer, and 3rd layer the coating nature of the above-mentioned constituent of ** and the smooth nature of a paint film obtained. An addition is usually 0.01 - 2% of the weight of a range to a constituent.

[0096] Any are sufficient, the plastics base material used for this invention -- transparence -- opaque -- this base material. For example, polycarbonate resin, such as poly (bisphenol-A carbonate), acrylic resin, such as a polymethylmethacrylate, a polyethylene terephthalate, Polyester resin, such as a polybutylene terephthalate and poly (ethylene -2, 6-naphthalate), Vinyl resin, such as a polyamide resin [of nylon 6 nylon 6, and 6 grades], polystyrene, polyacrylonitrile, and acrylonitrile-styrene copolymer, polyvinyl chloride, a poly 4-methyl pentene, and polypropylene, is mentioned. Acrylic resin, such as polycarbonate resin, such as poly bisphenol A carbonate, and a polymethylmethacrylate, is desirable, and poly (bisphenol-A carbonate) is especially more desirable than the usefulness of the covering effect obtained, the adhesive property to a base, etc.

[0097]

[Effect of the Invention] The protected plastic-molding object the front face of this invention obtained in this way. It consists of three-tiered structures which make the layer which makes react a sol gel reactant and the acrylic resin which has a hydroxyl and comes to heat-harden the 1st layer and the 2nd layer. And the contents of this sol gel reactant in each class are durable high abrasion resistance and the Plastic solid which scratches and has hardness and solvent resistance by increasing in order of the 1st layer, the 2nd layer, and the 3rd layer.

[0098] this moldings -- for example, apertures, such as an aircraft, a vehicle, and an automobile, and a headlight -- it can use for various in addition sheets [, such as a windshield and a face plate], such as apertures, such as buildings, such as a lens of a noise-proof wall and signal L.G.T.s, such as glasses and goggles, mirrors on curved roads, etc., such as lenses [, such as an aperture of a construction equipment] for optics, such as a lens, and a mirror, a house, a garage, a greenhouse, and an arcade, and

[0099]

[Example] Hereafter, although this invention is explained in full detail according to an example, this invention is not limited to this from the first. In addition, unless it indicates especially, the section and % mean weight criteria.

[0100]

[The examples 1-6 (example of acrylic resin A-F composition) of reference]

(Example of acrylic resin A-F composition)

a) It has a reflux condenser and churning equipment, and the 2-hydroxyethyl methacrylate (it omits Following HEMA) 13.1 section, MMA90.1 section, azobisisobutyronitril (it omits Following azobisisobutyronitril) 0.16 section and 1, and 2-dimethoxyethane 200 section was added, and it was made to dissolve into the flask which carried out the nitrogen purge. Subsequently, it was made to react to the bottom of 6-hour churning at 70 degrees C among a nitrogen air current. Reprecipitation refining of the obtained system of reaction was carried out by the weight ratio of n-hexane and isopropyl alcohol at 3:1 of mixed solvents, and the copolymer 95 section (acrylic resin-A) of the HEMA MMA composition ratios 10:90 (mole ratio) was obtained. The weight average molecular weight of this polymer was 100,000 from measurement of GPC.

[0101] Similarly, the copolymer (acrylic resin-B) of HEMA MMA composition ratios 30:70 (mole ratio) and the copolymer (acrylic resin-C) of 67:33 (mole ratio) were compounded. Weight average molecular weight was 200,000 and 60,000, respectively.

[0102] b) The copolymer 108 section (acrylic resin-D) of the HEMA FMA composition ratios 30:70 (mole ratio) was obtained like Above c except using the HEMA39.0 section, ethyl methacrylate (it omitting Following FMA) 80.1 section, azobisisobutyronitril 0.16 section and 1, and 2-dimethoxyethane 240 section. The weight average molecular weight of this polymer was 180,000.

[0103] c) The copolymer 108 section (acrylic resin-E) of the HPMA MMA composition ratios 30:70 (mole ratio) was obtained like Above b except using the 2-hydroxypropyl methacrylate (it omitting Following HPMA) 43.2 section, MMA70.1 section, azobisisobutyronitril 0.16 section and 1, and 2-dimethoxyethane 220 section. The weight average molecular weight of this polymer was 150,000.

d) The copolymer 95 section (acrylic resin-F) of the HEMA MMA composition ratios 20:80 (mole ratio) was obtained like Above a except using the 2-hydroxyethyl acrylate (it omitting Following HEMA) 23.2 section, MMA80.1 section, azobisisobutyronitril 0.16 section and 1, and 2-dimethoxyethane 200 section. The weight average molecular weight of this polymer was 150,000.

[0104] The **** for examining methods of the following [performance evaluation -- of a hardening paint film].

[0105] (1) Adhesive property -- put length with a knife, put a break into a test piece front face at intervals of 1mm wide, and form the 100 squares. After sticking a cellophane tape (tradename Scotch tape by Nichiban Co., Ltd.) on it, it pulled and exfoliated at a stretch in the direction of 90 degrees from the front face, and the number of the eyes which remained in the front face estimated the adhesive property. Therefore, full adhesion is meant 100/100 and full exfoliation is meant 0/100. (It is

based on JIS K5400)

[0106] (2) It scratched, and it was made to move to the front, forcing the heart which maintained the pencil at the angle of about 45 degrees to the test piece front face, and was made into the shape of a pillar by the hand of a hardness operating personnel, and the degree of hardness of the hardest pencil that does not get damaged in that case estimated. (It is based on JIS K5400)

[0107] (3) Abrasion resistance : using the Taber abrasion tester (Product made from an Oriental energy machine), on condition that wear ring CS-10F, 500g of loads, and 500 cycle, it wore out and the difference before and behind wear of the haze value called for from the following formula (delta haze value) estimated the test piece front face. (It is based on JIS K6735 or ASTM D1044)

[0108]

[Equation 1]

Haze value (%) = (a luminous diffuse transmittance - all light transmissions) x 100. [0109] (4) Abrasion-proof nature : after grinding a test piece front face against #0000 steel wool, viewing estimated the state where a front face got damaged, in the following five stages.

0: 1: which does not get damaged at all even if it grinds strongly -- 2: which will get damaged slightly if it grinds strongly -- 3: which will get damaged a little if it grinds strongly -- 4: which will get damaged if it grinds strongly -- even if it grinds weakly, get damaged [0110] (5) Priming-proof nature : the appearance-of-film change 2 hours or after boiling for 5 hours, an adhesive property, and abrasion-proof nature were evaluated for the test piece in tap water.

[0111] [Example 1]

(Constituent for the 1st layer) The methyl trimetoxysilane 4.0 section was put into the Erlenmeyer flask, and it added under churning, carrying out external intercooling of the solution which consists of the acetic-acid 0.4 section and the water 1.9 section. After continuing churning under a room temperature for about 1 hour, the isopropanol (it omits Following IPA) 12 section and the sodium acetate 0.04 section were added into this reaction mixture. Furthermore, churning was continued under the room temperature for about 24 hours. Subsequently, it dissolved in the mixed solvent which consists of the acrylic resin-A10 aforementioned section, the sec-butanol 45 section, and the methyl-ethyl-ketone (it omits Following MEK) 45 section in this reaction mixture, and filtered with the 1-micrometer filter, and the constituent 1-1 was prepared.

[0112] (Constituent for the 2nd layer) The methyl trimetoxysilane 30.5 section was put into the Erlenmeyer flask, and it added under churning, carrying out external intercooling of the solution which consists of the acetic-acid 3.0 section and the water 14 section. After continuing churning under a room temperature for about 1 hour, the isopropanol (it omits Following IPA) 20 section and the sodium acetate 0.3 section were added into this reaction mixture. Furthermore, churning was continued under the room temperature for about 24 hours. Subsequently, the solution which consists of the acrylic resin-B5.0 aforementioned section and the methyl-ethyl-ketone (it omits Following MEK) 27 section in this reaction mixture was added, and it dissolved. Subsequently, this solution was ripened for 24 hours, polysiloxane system paint additive PERENORU S4 (tradename: -- after Sannopuko) 0.2 section addition, it filtered with the 1-micrometer filter and the constituent 1-2 was prepared.

[0113] (Constituent for the 3rd layer) The acid distribution liquid which mixed the acetic-acid 3.5 section 30% beforehand in the methyl trimetoxysilane 30 section at the colloidal silica aqueosity distribution liquid (product made from Catalyst Chemicals Industry : tradename KATAROIDO SI- 30) 20 section was added, agitating violently under external intercooling. Subsequently, after continuing churning for bottom 3 hours of a room temperature, the IPA35 section and the sodium acetate 0.2 section were added. The pH value of this system was 5.3. After leaving it for three days at a room temperature, it filtered with the 1-micrometer filter and the constituent 1-3 was prepared.

[0114] (Manufacture of a Plastic solid, evaluation) 1-1 was applied with the wire bar of a constituent#20, and it was dried for 30 minutes at 120 degrees C after gentle placement for 20 minutes under the room temperature on the board with a thickness made of the poly (bisphenol-A carbonate) resin (it omits Following PC) of 3mm. The coating thickness film was 2.5 micrometers. Subsequently, the constituent 1-2 was applied with #50 wire bar on the coat front face of this layered product, and it heated for 20 minutes at 100 degrees C after gentle placement for 20 minutes under the room temperature. Coating thickness was 15 micrometers. Furthermore, on the cascade-screen front face, 1-3 were applied with the wire bar of a constituent#20, and they carried out heat hardening at 130 degrees C after gentle placement for 20 minutes under the room temperature for 1 hour. The coating thickness in this operation was 5 micrometers.

[0115] There was no crack in appearance, and the obtained Plastic solid was transparent and good. The cross cut adhesion test showed the good adhesive property by 100/100. The pencil degree of hardness was 4H, the Taber abrasion test was 1.8% of delta haze values, and the result of a steel wool examination was evaluation of 0, and was the surface hardness of a very high performance. Although it was under priming about this Plastic solid for 5 hours, an exterior change was not seen at all but the adhesive property was 100/100. Moreover, the result which ground the front face after being immersed against steel wool is evaluation of 0, and showed the outstanding priming-proof nature.

[0116] Moreover, a constituent 1-2 and 1-3 were stably used for coating, without gelling more than for one month.

[0117] On the other hand, in the PC board of the base material which has not prepared the protective layer, it was pencil degree-of-hardness 3B, the result of the Taber abrasion test was 48% of delta haze values, and the result of a steel wool examination was evaluation of 4.

[0118] The laminating of 2.5 micrometers of hardening layers of a constituent 1-1 and the 5 micrometers of the hardening layers of a constituent 1-3 was carried out one by one completely like the example 1 except not applying the aforementioned constituent 1-2 on a [example 1 of comparison] thickness 3mmPC board. This Plastic solid -- transparency -- it was smooth

and generating of a crack was not seen, either. Although the adhesive property was 100/100 in the cross cut adhesion test, the Taber abrasion test was 1.8% of delta haze values and the result of a steel wool examination was evaluation of 0, the pencil degree of hardness was F. Few [a paint film] white bluish marks were observed by being immersed in priming 2 hours, the crack generated this Plastic solid in the paint film in being immersed in 5 hours, and the fall of adhesion was also seen.

[0119] The PC-board Plastic solid to which the laminating of 2.5 micrometers of hardening layers of a constituent 1-1 and the 15 micrometers of the hardening layers of a constituent 1-2 was carried out one by one was obtained completely like the example 1 except not applying the [example 2 of comparison] aforementioned constituent 1-3. Although the adhesive property of this Plastic solid was 100/100 in the cross cut adhesion test and the pencil degree of hardness was 2H, the Taber abrasion test was 9% of delta haze values, and the result of a steel wool examination was evaluation of 2.

[0120] The PC-board Plastic solid to which the laminating of 15 micrometers of hardening layers of a constituent 1-2 and the 5 micrometers of the hardening layers of a constituent 1-3 was carried out one by one was obtained completely like the example 1 except not applying the [example 3 of comparison] aforementioned constituent 1-1. The adhesive property of this Plastic solid was 0/100 in the cross cut adhesion test. During measurement, the paint film exfoliated and the pencil degree of hardness and the Taber abrasion test have not been evaluated.

[0121] [Example 2]

(Constituent for the 1st layer) The methyl trimetoxysilane 4.0 section was put into the Erlenmeyer flask, and it added under churning, carrying out external intercooling of the solution which consists of the acetic-acid 0.4 section and the water 1.9 section. After continuing churning under a room temperature for about 1 hour, the IPA12 section and the sodium acetate 0.04 section were added into this reaction mixture. Furthermore, churning was continued under the room temperature for about 24 hours. Subsequently, it dissolved in the mixed solvent which consists of the acrylic resin-B18 aforementioned section, the sec-butanol 80 section, and the MEK80 section in this reaction mixture, and filtered with the 1-micrometer filter, and the constituent 2-1 was prepared.

[0122] (Constituent for the 2nd layer) The constituent 2-2 was prepared completely like the example 1 except using the acrylic resin-C5.0 section instead of acrylic resin-B.

[0123] (Constituent for the 3rd layer) The aforementioned constituent 1-3 was used.

[0124] (Manufacture of a Plastic solid, evaluation) The laminating of layer [3rd] layer [2nd] 5 micrometers per layer [the] and 20 micrometers and, and the 5.5 micrometers was carried out one by one on the PC board with a thickness of 3mm completely like the example 1. The obtained Plastic solids were 91.5% of all light transmissions, and appearance was transparent and good. The adhesive property was 100/100 in the cross cut adhesion test, the pencil degree of hardness was 5H, the result of the Taber abrasion test was 1.7% of delta haze values, and the result of a steel wool examination was evaluation of 0. As for this Plastic solid, change was not seen at all after the priming immersion test of 5 hours, as for appearance, an adhesive property, and surface hardness.

[0125] 2-1 was applied with the wire bar of a constituent#10, and it was dried for 30 minutes at 80 degrees C after gentle placement for 20 minutes under the room temperature on the polymethylmethacrylate (it abbreviates to PMMA) resin board with a [example 3] thickness of 2mm. The coating thickness film was 2.5 micrometers. Subsequently, the constituent 1-2 was applied with #40 wire bar on this coating film front face, and it heated for 20 minutes at 80 degrees C after gentle placement for 20 minutes under the room temperature. Coating thickness was 11 micrometers. Furthermore on this coating film front face, 1-3 were applied with the wire bar of a constituent#16, and they carried out heat hardening at 80 degrees C after gentle placement for 20 minutes under the room temperature for 4 hours. The coating thickness in this operation was 4 micrometers. The adhesive property of the obtained Plastic solid was 100/100, and surface hardness was pencil degree-of-hardness 7H, 2.4% of delta haze values of the Taber abrasion test, and evaluation of the steel wool examination 0. As for this coating film, change was not looked at at all by being priming immersed in 5 hours, either.

[0126] On the other hand, the surface hardness of PMMA which is a base material was pencil degree-of-hardness 2H, 29% of delta haze values of the Taber abrasion test, and the steel wool test evaluation 4.

[0127] [Example 4]

(Constituent for the 1st layer) The methyl trimetoxysilane 4.0 section was put into the Erlenmeyer flask, and it added under churning, carrying out external intercooling of the solution which consists of the acetic-acid 0.4 section and the water 1.9 section. After continuing churning under a room temperature for about 1 hour, the IPA12 section and the sodium acetate 0.04 section were added into this reaction mixture. Furthermore, churning was continued under the room temperature for about 24 hours. Subsequently, it dissolved in the mixed solvent which consists of the acrylic resin-D15 aforementioned section, the sec-butanol 68 section, and the MEK68 section in this reaction mixture, and filtered with the 1-micrometer filter, and the constituent 4-1 was prepared.

[0128] (Constituent for the 2nd layer) The methyl trimetoxysilane 28.5 section was put into the Erlenmeyer flask, and it added under churning, carrying out external intercooling of the solution which consists of the acetic-acid 3.0 section and the water 1.2 section. After continuing churning under a room temperature for about 1 hour, the IPA16 section and the sodium acetate 0.3 section were added into this reaction mixture. Furthermore, churning was continued under the room temperature for about 2 hours. Subsequently, the solution which consists of the acrylic resin-A6.0 aforementioned section and the MIBK42 section in this reaction mixture was added, and churning was continued further for 4 hours. Polysiloxane system paint additive PERI NORU-84 was filtered after 0.2 section addition and with the 1-micrometer filter, and the constituent 4-2 was prepared.

[0129] (Constituent for the 3rd layer) The acid distribution liquid which mixed the 40% colloidal silica aqueousity distribution liquid (product made from Catalyst Chemicals Industry - tradename KAT AROIDO SI- 40) 18 section, the water 3.6 section,

and the acetic-acid 4 section beforehand in the methyl trimetoxysilane 27 section was added, agitating violently under external intercooling. Subsequently, after continuing churning for bottom 24 hours of a room temperature, the IPA38 section and the benzyl trimethylammonium acetate 0.4 section were added. The pH value of this system was 5.2. After leaving it for two days at a room temperature, it filtered with the 1-micrometer filter and the constituent 4-3 was prepared.

[0130] (Manufacture of a Plastic solid, evaluation) The dip coating method was used on the PC board with a thickness of 3mm, and the laminating of layer [3rd] layer [2nd] 1.5 micrometers per layer [the] and 10 micrometers and, and the 5 micrometers was carried out one by one. As a result of evaluating the paint film performance of the obtained Plastic solid, the adhesive property was 100/100 in the cross cut adhesion test, the pencil degree of hardness was 3H, the result of the Taber abrasion test was 1.5% of delta haze values, and the result of a steel wool examination was evaluation of 0. As for this layered product, change was not seen at all after the priming immersion test of 5 hours, as for appearance, an adhesive property, and surface hardness.

[0131] By manufacture of the coating constituent for the [examples 5-6] 1st layer, it is the aforementioned acrylic resin instead of the aforementioned acrylic resin-A, - PC fabrication board was produced completely like the example 1 except using E or -E. As a result of evaluating the paint film performance of the obtained Plastic solid, the adhesive property was 100/100 in the cross cut adhesion test, the pencil degree of hardness was 4H, the result of the Taber abrasion test was 1.8% of delta haze values, and all of the result of a steel wool examination were evaluations of 0. As for this layered product, change was not seen at all after the priming immersion test of 5 hours, as for appearance, an adhesive property, and surface hardness.

[0132] [Example 7]

(Constituent for the 1st layer) To the constituent 1-1 used in the example 1, the constituent 7-1 was prepared completely like the example 1 except carrying out the addition dissolution of the Cymel 303 (methyl-ether type hexa methylol melamine resin) 1.0 made from Mitsui SATEKKU section, and the p-toluenesulfonic-acid 0.03 section further.

[0133] (Constituent for the 2nd layer) The constituent 2-2 was used.

[0134] (Constituent for the 3rd layer) The aforementioned constituent 4-3 was used.

[0135] (Manufacture of a Plastic solid, evaluation) The dip coating method was used on the PC board with a thickness of 3mm, and the laminating of layer [3rd] layer [2nd] 1.5 micrometers per layer [the] and 10 micrometers and, and the 3.5 micrometers was carried out one by one. As a result of evaluating the paint film performance of the obtained Plastic solid, the adhesive property was 100/100 in the cross cut adhesion test, the pencil degree of hardness was 3H, the result of the Taber abrasion test was 1.5% of delta haze values, and the result of a steel wool examination was evaluation of 0. Moreover, as for this paint film, after the priming examination of 5 hours was not changing at all.

[0136] [Examples 8-10] It is the aforementioned acrylic resin to the 2nd layer, respectively, - PC Plastic solid was produced completely like the example 1 except using D, -E, and -F. As a result of evaluating the paint film performance of the obtained Plastic solid, the adhesive property was 100/100 in the cross cut adhesion test, the pencil degree of hardness was 4H, the results of the Taber abrasion test were each delta haze value 1.7 and 1.6 or 1.6%, and all of the result of a steel wool examination were evaluations of 0. As for this layered product, change was not seen at all after the priming immersion test of 5 hours, as for appearance, an adhesive property, and surface hardness.

[0137] [Example 11]

(Constituent for the 1st layer) To the constituent 2-1 used in the example 1, the constituent 11-1 was prepared completely like the example 2 except carrying out the addition dissolution of the Cymel 303 (methyl-ether type hexa methylol melamine resin) 3.0 made from Mitsui SATEKKU section, and the p-toluenesulfonic-acid 0.1 section further.

[0138] (Constituent for the 2nd layer) The methyl trimetoxysilane 24.4 section was put into the Erlenmeyer flask, and it added under churning, carrying out external intercooling of the solution which consists of the acetic-acid 2.5 section and the water 12 section. After continuing churning under a room temperature for about 1 hour, the isopropanol (it omits Following IPA) 16 section and the sodium acetate 0.3 section were added into this reaction mixture. Furthermore, churning was continued under the room temperature for about 24 hours. Add the solution which consists of the Aldrich (Aldrich) poly (2-hydroxyethyl methacrylate) (viscosity average molecular weight 300,000 [about] 10.0 sections, and the ethanol 40 section in this reaction mixture, it was made to dissolve, and digestion was continued for further 24 hours. Polysiloxane system paint additive PERENORU S4 was filtered after 0.2 section addition and with the 1-micrometer filter, and the constituent 11-2 was prepared.

[0139] (Constituent for the 3rd layer) The constituent 1-3 was used.

[0140] (Manufacture of a Plastic solid, evaluation) The laminating of layer [3rd] layer [2nd] 2 micrometers per layer [the] and 15 micrometers and, and the 5 micrometers was carried out one by one on the PC board (3mm in thickness) like the example 1. As a result of evaluating the paint film performance of the obtained layered product, the adhesive property was 100/100 in the cross cut adhesion test, the pencil degree of hardness was 4H, the result of the Taber abrasion test was 1.6% of delta haze values, and the result of a steel wool examination was evaluation of 0. Moreover, as for this paint film, after the priming examination of 5 hours was not changing at all.

[0141] To the constituent 11-2 for the 2nd layer used in the [examples 12-13] example 11, PC Plastic solid was produced completely like the example 11 except carrying out the addition dissolution of the Cymel 303 (methyl-ether type hexa methylol melamine resin) 3.0 made from Mitsui SATEKKU section, the p-toluenesulfonic-acid 0.1 section (example 12) or the Cymel 370 (methyl-ether type hexa methylol melamine resin) 3.0 section, and the itaconic-acid 0.1 section (example 13) further, respectively. As a result of evaluating the paint film performance of the obtained Plastic solid, the adhesive property was 100/100 in the cross cut adhesion test, the pencil degree of hardness was 4H, the result of the Taber abrasion test was up

to 1.5 or 1.6% of delta haze values, and all of the result of a steel wool examination were evaluations of 0. As for this Plastic solid, change was not seen at all after the priming immersion test of 5 hours, as for appearance, an adhesive property, and surface hardness.

[0142] [Example 14]

(Constituent for the 1st layer) The aforementioned constituent 1-1 was used.

[0143] (Constituent for the 2nd layer) The aforementioned constituent 1-2 was used.

[0144] (Constituent for the 3rd layer) The tetramethoxy silane 20 section was dissolved in the IPA7 section, and it added further, agitating the centinormal hydrochloric-acid solution 10 section violently under external intercooling. Subsequently, after agitating under a room temperature for 3 hours, at 10 degrees C, it was left for 24 hours or more, and riped, and the sol gel reaction mixture of a tetramethoxy silane was prepared. The methyl trimetoxysilane 13.6 section was mixed in this sol gel reaction mixture 3 section, and the centinormal hydrochloric-acid solution 5.4 section was added, agitating violently under external intercooling. Subsequently, after agitating under a room temperature for 3 hours, the IPA8.9 section and 10% of sodium acetate acetic-acid solution 1.8 section were added. The pH value of this system was 5.2. After leaving it for three days at a room temperature, it filtered with the 1-micrometer filter and the constituent 14-3 was prepared.

[0145] (Manufacture of a Plastic solid, evaluation) 1-1 was applied with the wire bar of a constituent#20, and it was dried for 30 minutes at 120 degrees C after gentle placement for 20 minutes under the room temperature on the board with a thickness made from PC [] of 3mm. The coating thickness film was 2.5 micrometers. Subsequently, the constituent 1-2 was applied with #50 wire bar on the coat front face of this layered product, and it heated for 20 minutes at 80 degrees C after gentle placement for 20 minutes under the room temperature. Coating thickness was 15 micrometers. Furthermore, on the cascade-screen front face, 14-3 were applied with the wire bar of a constituent#20, and they carried out heat hardening at 120 degrees C after gentle placement for 20 minutes under the room temperature for 1 hour. The coating thickness in this operation was 4.5 micrometers.

[0146] There was no crack in appearance, and the obtained Plastic solid was transparent and good. The cross cut adhesion test showed the good adhesive property by 100/100. The pencil degree of hardness was 4H, the Taber abrasion test was 4.5% of delta haze values, and the result of a steel wool examination was evaluation of 0, and was the surface hardness of a very high performance. Although it was under priming about this layered product for 5 hours, an exterior change was not seen at all but the adhesive property was 100/100. Moreover, the result which ground the front face after being immersed against steel wool is evaluation of 0, and showed the outstanding priming-proof nature.

[0147] Moreover, a constituent 1-2 and 1-3 were stably used for coating, without gelling more than for one month.

[0148] [Example 15]

(Constituent for the 1st layer) The aforementioned constituent 4-1 was used.

[0149] (Constituent for the 2nd layer) The aforementioned constituent 4-2 was used.

[0150] (Constituent for the 3rd layer) In the tetrapod ethoxy silane 20 section, the centinormal hydrochloric-acid solution 7 section was added, agitating violently under external intercooling. Subsequently, after continuing churning for bottom 3 hours of a room temperature, at 10 degrees C, it was left for 24 hours or more, and riped, and the sol gel reaction mixture of a tetrapod ethoxy silane was prepared. The methyl trimetoxysilane 28 section was mixed in this sol gel reaction mixture 3 section, and the centinormal hydrochloric-acid solution 11.1 section was added, agitating violently under external intercooling. Subsequently, after agitating under a room temperature for 3 hours, the IPA18.5 section and 10% of sodium acetate acetic-acid solution 3.5 section were added. The pH value of this system was 5.2. After leaving it for three days at a room temperature, it filtered with the 1-micrometer filter and the constituent 15-3 was prepared.

[0151] (Manufacture of a Plastic solid, evaluation) The dip coating method was used on the PC board with a thickness of 3mm, and the laminating of layer [3rd] layer [2nd] 1.5 micrometers per layer [the] and 10 micrometers and, and the 5 micrometers was carried out one by one. As a result of evaluating the paint film performance of the obtained Plastic solid, the adhesive property was 100/100 in the cross cut adhesion test, the pencil degree of hardness was 3H, the result of the Taber abrasion test was 4.2% of delta haze values, and the result of a steel wool examination was evaluation of 0. Moreover, as for this Plastic solid, change was not seen after the priming immersion test of 5 hours, as for each of appearance, adhesive properties, and surface hardness.

[0152] [Example 16]

(Constituent for the 1st layer) The aforementioned constituent 7-1 was used.

[0153] (Constituent for the 2nd layer) The aforementioned constituent 4-2 was used.

[0154] (Constituent for the 3rd layer) The tetramethoxy silane 20 section was dissolved in the IPA3 section, and it added further, agitating violently the acetic-acid 2 section and the water 12 section under external intercooling. Subsequently, after agitating under a room temperature for 3 hours, at 10 degrees C, it was left for 24 hours or more, and riped, and the sol gel reaction mixture of a tetramethoxy silane was prepared. The methyl trimetoxysilane 6 section was mixed in this sol gel reaction mixture 3 section, and the acetic-acid 0.6 section and the water 3.0 section were added, agitating violently under external intercooling. Subsequently, after agitating under a room temperature for 3 hours, the IPA4 section and the benzyl trimethylammonium acetate 2 section were added. After leaving it for six days at a room temperature, it filtered with the 1-micrometer filter and the constituent 16-3 was prepared.

[0155] (Manufacture of a Plastic solid, evaluation) The dip coating method was used on the PC board with a thickness of 3mm, and the laminating of layer [3rd] layer [2nd] 1.5 micrometers per layer [the] and 10 micrometers and, and the 3.5 micrometers was carried out one by one. As a result of evaluating the paint film performance of the obtained Plastic solid, the

adhesive property was 100/100 in the cross cut adhesion test, the pencil degree of hardness was 3H, the result of the Taber abrasion test was 3.2% of delta haze values, and the result of a steel wool examination was evaluation of 0. Moreover, as for the paint film of this Plastic solid, after the priming examination of 5 hours was not changing at all.

[Translation done.]